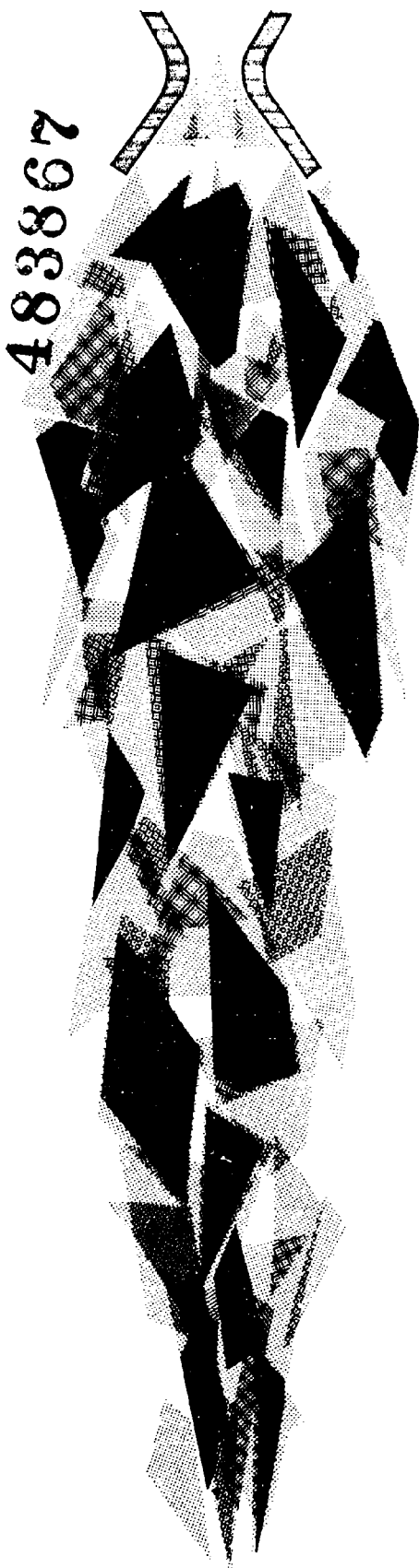


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REPORT NO. S-101

LITERATURE SEARCH ON METHODS
OF PARTICLE SIZE MEASUREMENT

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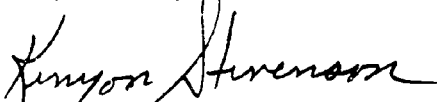
Report No. S-101

LITERATURE SEARCH ON METHODS OF PARTICLE SIZE MEASUREMENT

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LITERATURE SEARCH ON METHODS OF PARTICLE SIZE MEASUREMENT

ABSTRACT

A survey of the literature on methods of determination of the particle size of fine powders was performed. A summary of the information obtained is presented and a number of pertinent articles are reviewed in detail. The scope of the survey was limited to measurement in the sub-sieve range and involved primarily those methods of interest in the solid propellant field for measuring ammonium perchlorate. An appendix is included which lists additional references which may be of interest to persons concerned with the size of fine powders.

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GLOSSARY

A capsule description of some of the particle size apparatus referred to in the report is included at this point. Additional information may be obtained from The Analyst, 88, pp. 156-187, or from the various manufacturers.

Andreasen Pipette

A sample is dispersed in approximately 600 ml. of liquid. A 10 ml. sample is withdrawn, using a fixed pipette, from a point approximately 20 cm. below the surface, at varying time intervals. The weight of solids in each sample is determined after evaporation of the liquid. The size distribution is calculated from the fall time and distance using Stokes' Law.

Cenco Photelometer

See turbidimetric methods.

Coulter Counter

This apparatus measures the change in resistance as particles suspended in an electrolyte pass through an aperture having an electrode on either side. The change in resistance is proportional to the particle volume.

Eagle-Pitcher Turbimeter

See turbidimetric methods.

Fisher Sub-Sieve Sizer

This is one of several air permeability methods. Dried air is passed through a packed bed of the material to be measured. The pressure drop across the bed is converted into a surface area value using one of a family of curves supplied with the instrument. The powder density and porosity of the bed are used in selecting the proper curve.

Flying-Spot Particle Size Resolver

A moving spot of light is focused on the sample to be measured. The amount of light passing through the sample varies with the size of the particle. The changes in intensity are fed into electronic counting and sizing circuits. A memory device keeps each particle from being counted more than once.

Micromerograph

The Micromerograph is an air sedimentation device in which the particles are dispersed and injected into the top of a column by compressed nitrogen. The particles settling to the bottom are weighed by an automatic balance. The weight settled as a function of time is converted to a particle size distribution by means of templates based on Stokes' Law.

Mine Safety Appliances Particle Size Analyzer

This is a liquid sedimentation technique in which a dispersion in one liquid is placed in a settling tube on top of a liquid of somewhat greater density. The rate of sedimentation through the second liquid is determined by measuring the volume of sediment at various time intervals. Size distribution is calculated from Stokes' Law.

Nitrogen Adsorption

The amount of nitrogen adsorbed in a sample is determined by measuring the pressure exerted by known volumes of gas at a constant temperature. The data are used to compute a surface area using either the adsorption theories of Brunauer, Emmett and Teller (BET) or Harkins and Jura (HJa-absolute or HJr-relative).

Turbidimetric Method

A beam of light is passed through a dispersion of particles settling in a liquid medium. The change in light transmission, which varies with particle size and concentration, is measured as a function of time. These data are converted into a size distribution using Stokes' Law.

LITERATURE SEARCH ON METHODS OF PARTICLE SIZE MEASUREMENT

1. INTRODUCTION

The measurement of the size and size distribution of fine powders is not a simple problem. Several books have been written on the subject and considerable work has been done at various research and development laboratories. The solid propellant industry is generally concerned with measuring the size distribution of oxidizers, usually ammonium perchlorate, between the limits of 1 and 400 microns. The upper portion of this range, above 100 microns, is usually determined by screening and is seldom difficult. Accurate measurement in the 1 to 100 micron range is frequently difficult with any material and is especially troublesome with environmentally sensitive materials like ammonium perchlorate.

In preparation for a concerted study of ammonium perchlorate, part of which will be devoted to studying the effect of oxidizer size on burning rate, a search of existing literature on particle size measurement was performed.

Bibliographies on the subject of particle size measurement were obtained from Redstone Scientific Information Center and from the Defense Documentation Center. In addition Chemical Abstracts was searched over the period of 1947 through 1965. Articles under the subject headings of particle size and sedimentation were investigated. The articles which contained pertinent information were reviewed in detail under four headings:

- (1) Surveys of Methods for Particle Size Determination
- (2) Evaluations of the Sharples Micromerograph
- (3) Evaluations of the Coulter Counter
- (4) Treatment of Particle Size Data

In addition, a number of references in Chemical Abstracts which were not reviewed in detail are listed in an appendix. The appended material consists primarily of references not readily obtainable and of

material dealing with methods and particle sizes which are not of immediate interest in the solid propellant field. Some of these articles may be of interest to others involved in size measurement.

Experimental work on improving size measurement techniques, primarily with the Micromerograph, and on establishing the limitations and reliability of the data is in progress and will be continued. A comprehensive correlation of the pertinent size criteria with propellant burning rates is planned, and these results will be published in subsequent Special Reports. An attempt will be made in these reports to compare results obtained at this installation with data reported by others in the solid propellant field.

2. SUMMARY

This report summarizes the current state-of-the-art of particle size measurement and data treatment as applied to measurement of ammonium perchlorate particle size distributions. The information logically falls into the following categories. First, a number of comprehensive surveys of size measurement techniques are reviewed. Second, evaluations of two particular instruments commonly proposed for determining particle size distributions in the solid propellant field, the Micromerograph® and the Coulter Counter®, are summarized. Last, methods of treatment of particle size data are considered.

2.1 Surveys of Methods for Particle Size Determination

Use of the Ro-tap or other mechanical devices has been found satisfactory for materials such as ammonium perchlorate down to particle diameters of 50 to 100 microns, depending upon the experimenter. The Alpine Jet Sieve was found by several authors to be effective down to about 20 microns.

The methods for measuring particles below this size are many and varied. They may be categorized as follows.

- (1) Microscopic, including automated systems such as the "Flying Spot Particle Resolver."
- (2) Liquid sedimentation, the Andreasen Pipette and the MSA Particle Size Analyzer are two of the most popular.
- (3) Air sedimentation, the Micromerograph.
- (4) Turbidimetric, actually a variety of liquid sedimentation.
- (5) Electrical resistivity, the Coulter Counter.
- (6) Air classification.

Two other techniques which supply single values only, are air permeability (the Fisher Sub-sieve Sizer) and the BET adsorption technique (applying the unified adsorption theory of Brunauer, Emmett and Teller). The former measures an "external" surface or a "surface envelope" while the latter measures a "total" surface.

All six of the size distribution methods listed had one problem in common, that of adequately dispersing the particles without inducing grinding. In addition, the microscopic methods had the limitation of using only a small sample, thereby increasing the possibility of an error due to sampling. All of the sedimentation methods relied on the concept of a "Stoke's diameter," that is the diameter of a sphere having the same terminal velocity as the particle being measured. Generally the microscopic and liquid sedimentation methods (especially the Andreasen Pipette) were considered to be "absolute methods" although they were too time consuming for control purposes. The MSA Analyzer had the normal dispersion difficulty plus the problems of (1) sampling of the dispersion, (2) transfer of the dispersion to the settling chamber, and (3) use of two liquids of different densities for each material tested. The turbidimetric method seems to give excellent results, though it was used by only two of the authors and has the same dispersion difficulty as the other methods. The Micromerograph and Coulter Counter are discussed separately.

2.3 The Sharples Micromerograph

Nine of the articles reviewed, eight different authors, dealt in large part with the Sharples Micromerograph. Most of the opinion was quite favorable. The advantages most frequently mentioned were those of:

- (1) Simplicity and ease of operation.
- (2) Economy of operator time.
- (3) Reproducibility (especially within a single instrument).

The disadvantages of the Micromerograph reported by most authors were:

- (1) Low recovery of charged sample.
- (2) Electrostatic charge on particles (associated with low recovery).
- (3) Variations between instruments.
- (4) Lack of accuracy.

Probably the most common criticism of the Micromerograph was the low recovery of the material charged. Recoveries generally ranged from 30% to 50%. Most authors stated that the unrecovered material was predominately fine, while others stated that it was representative of the

original charge or coarse particles. Certainly more confidence would be placed in the results if recoveries could be raised to 75% or better.

A probable reason for the low recovery was that of electrostatic charge on the particles, causing them to be attracted to the walls of the column. Several installations used X-ray radiation to alleviate these static forces, but no data for evaluation of the results were found. The use of a radiation source or a radioactive gas has also been proposed.

Several authors have discussed the variations between instruments on a given sample. The least discrepancy between instruments was reported by L. R. Phillips (3.2.8), in work on UO_2 . Three instruments were used at the same facility which gave quite similar results, although the authors thought the difference was significant. In most of the other cases there was little or no information on deagglomerator conditions, so little significance can be attached to their comparison of several instruments.

The accuracy, as differentiated from reproducibility, of the Micromerograph was questioned by three of the authors. However, in none of their reports was there a valid comparison with a "standard method" by which to judge the accuracy of the Micromerograph.

In general, it appears that the Micromerograph, provided that frequent calibration checks are performed, is a good, reproducible instrument for size measurement. The operator time involved is less than most methods, and the calculations are not complicated. The results obtained are not necessarily an absolute measure of particle size. Microscopic examination is desirable as a check on the actual particle size and to determine the effect of deagglomeration. A means of increasing the recovery of the sample is highly desirable. A source of ionization or use of a conductive gas should work if the problem is static attraction.

2.3 The Coulter Counter

One of the newest methods of particle size determination uses the change in electrical resistance, caused by particles suspended in an electrolyte, as a means of determining particle volume. One instrument based on this principle is the Coulter Counter. Five articles were reviewed

which dealt with use of the Coulter Counter for size determination. Only two of these had success in matching Coulter Counter results with an "absolute" method. One of these required use of a "correction factor" which was determined experimentally. Two of the authors were not able to obtain data appearing to have any validity at all, and the other author made no attempt to compare Coulter Counter data with any standard. Two of the authors reported that the standard ragweed pollen used for calibration changed size during their experiments. Apparently the problems are:

- (1) Maintaining sufficiently clean air and slurries.
- (2) Finding an electrolyte which will not dissolve ammonium perchlorate.
- (3) Maintaining constant temperature.
- (4) Eliminating electrical noise and interference.
- (5) Establishing an adequate calibration technique.

2.4 Treatment of Particle Size Data

There were three common methods of treating particle size data: arithmetic-normal; log-normal; and the Rosin-Rammler relationship. The articles reviewed were nearly unanimous in stating that particle size distributions, especially when achieved by grinding, are logarithmically normal. A homogeneous distribution then should plot as a straight line on log-probability paper and should be symmetrical when plotted as cumulative or incremental frequency curves on semi-log paper. In practice heterogeneous or bimodal distributions were frequently observed. These were treated by several of the authors, especially Kottler (3.4.4) and Irani (3.4.5), who discussed techniques for separating heterogeneous distributions into their log-normal components.

3. DISCUSSION

The articles which were considered to be of immediate interest insofar as measurement of ammonium perchlorate particle size is concerned are summarized below. For convenience the discussion of these articles has been divided into the same four categories as was the Summary section.

3.1 Surveys of Methods for Particle Size Determination

- 3.1.1 A comparative Study of Methods for Particle Size Analysis in the Sub-sieve Range, by H. F. Fischmeister, C. A. Blande, and S. Palmquist, Powder Metallurgy, 4, No. 7, pp. 82-110 (1961).

This study was an interesting survey of a number of methods for particle size analysis. The methods included sieving, microscopic, Fisher Sub-Sieve Sizer, turbidimetric, and Micromerograph. Determinations on some 13 different powders ranging in median size from ~2 to ~50 microns were made by some of the methods. Equivalent surface diameters were determined from Fisher Sub-Sieve and BET methods. These were compared with equivalent surface diameters calculated from size distributions. In this comparison it was illustrated that the Fisher and BET methods measured different characteristics of the powders, for example exterior and total surfaces. One puzzling feature was that the equivalent surface diameter calculated from the size distribution varied widely and inconsistently from the weight median size for some of the powders. No explanation was given. The authors considered the Micromerograph to be good method, agreeing very well with a liquid sedimentation balance, the turbidimetric measurement and a centrifugal classifier for a nominal 15 micron silica powder. Again, good agreement was noted among seven methods for a nominal 15 to 20 micron tungsten carbide powder with the exception that the Micromerograph, microscopic, and turbidimetric methods showed small amounts of very coarse particles not indicated by the other methods. This was attributed to the presence of large agglomerates, somewhat resistant to mechanical working, but which were broken up during the preparation of dispersions for the other methods.

The authors were apparently impressed by the ingenuity of the deagglomeration technique for the Micromerograph. They did, however, in one case find the Micromerograph to indicate a considerably finer distribution than did the other methods. This was attributed to fragmentation during deagglomeration. This particular material, WO_3 , was considered to have a strong tendency to fragment. There was no discussion of the suggested technique for determining optimum deagglomeration by the Micromerograph. There was a very interesting section on the "true" size distribution of a powder in which the authors discussed the difficulty of determining the point at which deagglomeration ended and grinding, or discrete particle size reduction, began. The only conclusion drawn was an opinion that it was highly improbable that complete deagglomeration could ever be achieved without some grinding of particles. They stated that in practice the essential requirements for size analysis of fine powders, having a strong tendency toward agglomeration, were reduced to those of: (1) reproducibility, and (2) sensitivity to changes that affect the proposed use of the material. The sensitivity of the analysis to a given change in the powder characteristics must be greater than the sensitivity of the process. Then variations of powder quality that affected product quality would be detected with certainty.

The final section of this paper reported a series of tests run on a tungsten carbide powder in which samples were taken after various periods of grinding in a ball mill. Particle sizes were measured by turbidimetric means, Micromerograph, air permeability, gas adsorption and several other methods. It was shown that the Micromerograph followed the decreasing size reasonably well to a size of about two microns (median), at which point it failed to indicate further reduction in particle size. The settling time for two micron tungsten carbide corresponds to 10 micron ammonium perchlorate. These results indicate that below 10 microns the Micromerograph may become insensitive to ammonium perchlorate size changes. This article is suggested reading for anyone interested in particle size measurement. 63 references.

3.1.2 Particle Size Analysis, by B. Scarlett, Chemical and Process Engineering, 46, No. 4, pp. 197-201 (1965).

This article referred to a listing, classification and description of 74 methods of particle size determination, The Analyst, Vol. 88 (1963), and indicated that this comprehensive classification was the first stage of a committee's work. References were given to three major symposia in 1947, 1954, and 1958, and to a coming symposium in 1966. Little or no specific information was included in this paper. There was reference to the Coulter Counter as "probably the most significant advance in particle sizing in the last decade" which "unlike most new instruments, employed a completely new physical principle in particle sizing which is nevertheless simple and elegant." A significant statement in this regard was that there is a tendency to regard such an instrument as a "black box" which will automatically produce the right answer. This tendency certainly should be avoided. 56 references.

3.1.3 Comparison of Methods for Particle Size Analysis, by J. A. Freitag, National Lead Company of Ohio, Cincinnati, Ohio, NLCO 925, September 30, 1964.

The paper was based on work performed for the Atomic Energy Commission.

Abstract (by author) "A comparison was made of methods of particle size analysis applied to uranium trioxide, uranium tetrafluoride, and magnesium fluoride. The methods studied were the Coulter Counter, sedimentation (in liquid by the Andreasen pipette and in nitrogen by the Micromerograph) and direct measurement from photographs.

Satisfactory agreement among the methods was observed for materials containing spherical shaped particles; however, deviations between the Coulter method and sedimentation methods were found for irregular shaped particles."

Summary

The article discussed the theory of the Coulter Counter, and sedimentation theory, including the maximum size for which sedimenta-

tion was valid. The Micromerograph template was compared with this maximum size and the template indicated a capability for measuring particles approximately 10 times the maximum size for which Stoke's Law holds. However, it was stated that the template was corrected for this oversize material.

The author concluded that the Coulter Counter gave an accurate measure of particle volume quickly and accurately. He also concluded that "when rod-shaped particles fall in a sedimentation method, they turn to their most stable position, which is the one offering the greatest resistance to fluid flow. In so doing the particles will drift sideways and approach the wall of the container introducing an error from this source. This wall effect seems quite pronounced in the Micromerograph where up to about 70% of the sample is found to stick to the side of the wall." The author quoted L. R. Phillips (see Section 3.2.8) as stating that it was "inherent in the Micromerograph type of sedimentation measurement that a true particle size distribution is not directly obtained, but the results are biased in the direction of coarse particles." Mr. Freitag presented data on three materials. One of these he classified as an ideal sample of discrete, nearly spherical particles with little tendency to either agglomerate or fracture. With this sample all methods agreed well except the microscopic count, which appeared to give a median somewhat larger than the others. The author indicated that this was expected, since a particle would normally lie on its most stable surface, exposing a broader area to the observer.

The next particle studied was magnesium fluoride, a "poor" material, since the particles were oblong and needle shaped. The Coulter Counter and Andreasen pipette both showed coarser distributions than the Micromerograph. The photomicrograph showed a considerably larger distribution even though the measurement was made across the narrow part of the elongated particle. The author attributed this discrepancy to particle orientation on the slide, although it seems more likely that each of the other methods fragmented the long needles. The third material was a uranium oxide which was described as agglomerates of smaller particles. The author stated that the Micromerograph was believed to have fractured the sample and caused a

large increase in fine material. A microscopic examination of the material taken from the Micromerograph pan revealed a large proportion of needle-shaped particles which, according to the author, fell slower than expected and appeared smaller than they were. A Coulter Counter determination on this Micromerograph pan material gave a median size of approximately 5 microns as compared with an approximately 15 micron median on the original sample by Coulter Counter. The author concluded, among other things, that the Micromerograph, being especially designed to break up agglomerates, would give results which might be difficult to interpret with frangible materials. He suggested the use of microscopic examination for dispersion and particle shape in order to interpret the results correctly.

3. 1. 4 Use of Alpine Air-Jet Sieve, Tyler Ro-Tap and Micromerograph to Determine Particle Size of Ammonium Perchlorate, by Emery H. Willes, et. al., Thiokol Chemical Corporation, Brigham City, Utah. Bull. 17th Meeting, JANAF Panel on Anal. Chem., Sept. 1961, pp. 11-25 (Report classified; paper unclassified).
Abstract (by authors)

"A method has been developed to provide rapid and accurate information on particle size distribution of ammonium perchlorate. A primary value of this method at Thiokol is in quality control of the oxidizer grinding operation during the manufacture of solid propellant fuel for rocket engines. Use was made in this work of the recently developed Alpine Air-Jet Sieve test equipment, which employs a novel vacuum sieving and mixing technique.

Particle size distributions were determined for several ammonium perchlorate materials, using Micromerograph, Alpine, and Tyler Ro-Tap test equipment. The average relative deviation between the Alpine and Tyler Ro-Tap methods of test was found to be 4.0 percent in the 44-150 micron particle size range. Between the Alpine and the Micromerograph in the 25-44 micron particle size range, the average deviation was found to be 4.6 percent."

Summary

It was concluded that approximately three minutes sieving time was adequate with the air-jet sieve even with cadmium stearate, a waxlike material which clogs easily. Data were presented to indicate that 20 minutes and longer was required for vibrating or shaking screens. The Alpine, Tyler Ro-Tap and Micromerograph data presented in the report for ammonium perchlorate agree remarkably well.

- 3.1.5 Methods for Determining the Particle Size and Surface Area of Small Particles, by J. R. Sulcer and J. R. Denson, Thiokol Chemical Corporation, Huntsville, Alabama. Bull. 17th Meeting, JANAF Panel on Anal. Chem., Sept. 1961, pp. 1-9 (Report classified; paper unclassified).

Abstract (by authors)

"A brief review is presented of the various methods for determining particle size and specific surface of small materials. Emphasis is placed on the measurement of surface area by nitrogen adsorption. The use of techniques employing the gas chromatograph to measure the volume of gas adsorbed is discussed in some detail. Experimental data are presented from the determination of the specific surface of ferric oxide, aluminum powder, carbon black, ground ammonium perchlorate, and p-quinone dioxime."

Summary

Advantages and disadvantages of a number of size determination methods were discussed, including the Sharples Micromerograph. The only thing of significant interest was that Dr. Sharples was again actively engaged in perfecting the Micromerograph and that this instrument should become a more useful tool in the future.

Surface area by gas adsorption using a Perkin-Elmer 154-C chromatograph was discussed. Nitrogen was adsorbed on the sample from a gas stream of helium and nitrogen, producing an adsorption peak on the chart record indicating the difference in composition between the entrance and exit gas mixtures. The gas eluted on warming the sample produced a desorption peak of equal area. Experimental procedures and data were

described in detail indicating satisfactory results, for instance with ammonium perchlorate sizes having specific surfaces of approximately 5,000 cm²/gm.

- 3.1.6 Evaluation of the Cintel Flying-Spot Particle Resolver, by E. A. Luster, et al., U. S. Naval Propellant Plant, Bull. 17th Mtg., JANAF, Panel on Anal. Chem. Sept. 1961, pp. 27-34 (Report classified; paper unclassified).

Abstract (by authors)

"The principles and possible applications of the Flying-Spot Particle Resolver are discussed. Data are presented for particle size determination by the Micromerograph, microscope, and Flying-Spot Particle Resolver. Preliminary results indicated that this instrument could be applied to particle size measurements of aluminum and other dimensionally stable materials, but because of aggregation in the sample would not offer any advantages over the Micromerograph for use with ammonium perchlorate."

Summary

Considerable details on the Flying-Spot Particle Resolver were given along with data on the three methods for a nominal 36 micron carborundum sample. Micromerograph recoveries were high and the median sizes by all methods were essentially identical. It appeared, however, that the size distributions did not agree either between methods or between the two Micromerographs which were used. Data on nominal seven micron aluminum were reported which showed relatively low recoveries on the Micromerographs. There was good agreement on median size between the Micromerograph and Flying-Spot sizer.

However, for ammonium perchlorate the Micromerograph data varied widely between instruments and on different runs with a given instrument. No data were given on the deagglomerator settings. The authors indicated that two Micromerographs operated under standard conditions do not agree on ammonium perchlorate and that under the same or varying conditions any given Micromerograph may not agree with itself. However, the authors did not include sufficient data on their Micromerograph determinations to indicate that they investigated the optimum deagglomerator setting

or that the Micromerographs were set at the same values. Indeed, they indicated that a median of 46.4 microns could be reduced to 11 by changing the Micromerograph settings. This is easily understandable and emphasizes the need for extreme care in selecting deagglomerator conditions and the importance of reporting the settings along with the size data.

- 3.1.7 Particle Size and Surface Area by Micromerograph, Sorptometer and Microscopic Measurements, by C. H. Johnson, et al., Alleghany Ballistics Laboratory, Bull. 19th Mtg. ICRPG, Working Group on Anal. Chem., Nov. 1963, pp. 265-269 (Report classified; paper unclassified).

Particle sizes were determined using a Micromerograph, Sorptometer, and microscope. An ammonium perchlorate particle size distribution was determined by Micromerograph and microscopic methods and found to represent a straight line on log probability paper. The microscopic data, presented as a number distribution, were converted to a weight median of 8.9 microns. This compared with the Micromerograph median of 12.2 microns. Surface areas, as calculated from these two methods for a number of aluminum and ammonium perchlorate samples, were compared with Sorptometer measurements. The Sorptometer data were higher in a majority of the lots tested. This was attributed to porosity and irregularity of the particles. The microscopic and Micromerograph results were frequently close, with the microscope yielding higher areas in most cases. The size distributions data were not reported. It would have been informative to have had these data in addition to the calculated areas.

- 3.1.8 Comparison of Recent Methods for Particle Size Measurement of HMX, by Harry L. Stalcup, Naval Propellant Plant, Bull. 19th Mtg. ICRPG, Working Group on Anal. Chem., Nov. 1963, pp. 271-276 (Report classified; paper unclassified).

Particle sizes of HMX were obtained using the Coulter Counter, Micromerograph, and Cenco Photometer. Comparisons were first made with standard glass beads, supplied by the Sharples Company, on the Micromerograph and Coulter Counter. The two methods gave essentially

equivalent data except that the Coulter Counter indicated an over abundance of particles at the small particle end of the curve. The median value obtained for HMX by the Micromerograph was smaller, 13.5 microns as opposed to 16 microns, than that obtained with the Coulter Counter. The samples, however, had received different treatments, and this could well be the reason for the difference in size. As with the glass beads the log-normal plots of the data indicated an abundance of large particles in the Coulter Counter data. Also, a deficiency of large particles in the Micromerograph data was noted. The microscopic data indicated median value of 35 microns, disagreeing greatly from the other two methods. Of the 1,006 particles counted, only ten were larger than 20 microns, but these ten particles accounted for 90 % of the weight. This fact illustrated the extreme sensitivity of the microscopic results to a few large particles and emphasized the danger of using this technique as a standard of comparison for other methods. The seven figures referred to in the paper did not appear in the Bulletin. Their inclusion would have made the paper more informative.

3.1.9 Particle Size Measurement and the Effect of Particle Size on the Burning of Chemical Delay Compositions,
by D. R. Eigsti and R. D. Dwiggins, U. S. Naval

Ordnance Laboratory, NAVWEPS Report 7304, Nov. 16, 1960.

Several methods of determining particle size were discussed briefly. Among these were microscopic, Coulter Counter, elutriation, and several liquid sedimentation techniques. A turbidimetric method using the Eagle-Pitcher Turbimeter was discussed in detail. Determinations on four sizes of tungsten powder were made using the turbimeter, Micromerograph, and Coulter Counter. Surface area was measured using a BET apparatus. The turbimeter and the Micromerograph gave similar results. The Coulter Counter weight median diameters were about 4 or 5 times the diameters by the other methods. The authors thought that the turbimeter was an accurate, reproducible instrument. No reproducibility data were included for the Micromerograph, but the authors did not like it because of the low recoveries. The results from the Coulter Counter were considered not to be indicative of

the size of the sample. The Coulter analysis was performed at Coulter Electronics' own laboratories. A description was given of a microscopic method, but no data were reported.

3.2 Evaluations of the Sharples Micromerograph

3.2.1 The Micromerograph, The New Instrument for Particle Size Distribution Analysis, by Dr. F. S. Eadie and Dr. R. E. Payne, British Chemical Engineering, 1, pp. 306-311 (1956).

This article was written by two investigators from Sharples Research Division and is essentially a description of the Micromerograph written at about the time of its introduction. No disadvantages of the Micromerograph are discussed. The authors state that the Micromerograph will indicate details of the particle size distribution which are undetectable by liquid sedimentation or microscopic examination techniques.

3.2.2 Particle Size Measurement with a Micromerograph, by J. R. May, Chemical Engineering Section, Australian Atomic Energy Commission, Mining and Chem. Eng. Rev., 43, pp. 46-49 (1951).

This article discussed the Sharples Micromerograph and included a description and presentation of data illustrating the determination of optimum deagglomeration settings and typical size distributions. The materials measured had medians ranging from approximately 3 to 20 microns. (The 3 micron material was red lead and had a high particle density.) Of significant interest was the author's statements referring to holdup in the column. He reported recoveries ranging from 33 to 55%. He also stated that the material sticking to the wall is representative of the original sample. He stated that samples taken from both the wall and the pan after a run was completed had the same size distribution as the original powder. No mention was made, however, of the methods of obtaining the sample from the wall, and no data on the size distribution determination was included in the article.

The author stated that reproducible results could be obtained and that where any lack of reproducibility had shown up, it had been

invariably traced to poor sampling techniques. He indicated a need for thorough mixing of the original sample. He also stated that the Micromerograph is ideally suited for rapid routine size analysis, that reproducible deagglomeration can be assured, and that very little maintenance was needed in three years of operation. He did indicate that the electronic apparatus needed occasional attention and that the surfaces of the deagglomerator had to be replated within a three year period because of slight wear at the apex.

3.2.3 Particle Size Determination by the Sharples Micromerograph, by D. J. Bullock and H. C. Grant, Explosives Research & Development Establishment, Waltham Abbey, Essex, England, TM No. 16/ M/ 61 (1961).

Abstract (by authors)

"The theory and operational technique of the Sharples Micromerograph are described. An investigation has been carried out to assess its efficiency as an automated weight sedimentometer for the evaluation of weight/ size distribution of particulate materials. Results show that its accuracy is reduced by failure to sediment the whole of the powder under test, this effect being accentuated in the case of most fine powders. The instrument cannot be used satisfactorily for control work unless electrostatic charging of the sedimenting material is eliminated and a modification is suggested."

Summary

The principle of the Micromerograph was discussed at length and four phases of experimental work were reported:

- A. Establishment of the "most representative distribution curves" for materials.
- B. Measurement of the effect on indicated size distribution of loss of powder to the walls of the sedimentation column.
- C. Evaluation of reproducibility of the results.
- D. Determination of the ability of the instrument to differentiate between samples of the same powder, each possessing slightly different surface areas.

In the first phase a series of curves, obtained at varying deagglomerator settings and including the "most representative curve," was

illustrated for chromium sesquioxide and ammonium picrate. The deagglomerator settings used to determine these curves were not included. The author believed that at complete deagglomeration, increase of the shear force would not move the distribution curve in the fine direction. It appears that in determining this "most representative" curve, considerable grinding may have occurred.

Micromerograph runs were made on a large number of materials. No "standard" size measurement was included for comparison, but the specific surface areas were given. The report indicates that these were determined by air permeability. The percent recoveries were tabulated, many materials having less than 50% recovery. To investigate this loss of material during sedimentation the authors collected material from the balance pan from several runs and determined the particle size of the material recovered. Data are presented for aluminum powder and copper chromate. The aluminum powder (median size 20 microns) showed no change on the second pass through the Micromerograph, but a definite loss of fines was illustrated in the 3rd pass through the column. The copper chromate (median size approximately 5 microns) showed large changes in size distribution upon each pass through the column. This distribution was bimodal, the first determination showing approximately 76% of a material with a median of 5 microns and 24% with a median of approximately 60 microns. On the second pass the median of the smaller distribution was essentially unchanged but its quantity was reduced to 58% of the composite. Upon the 3rd pass the median again was essentially unchanged but it was reduced to 44% of the total. It appeared, then, that either through adherence to the column walls or through loss of these fine particles when recovering the pan material, this very fine distribution was being lost.

Samples of APC (original median of approximately 2 microns) and of titanium dioxide (median of approximately 20 microns) were tested at intervals of a week or so. The APC showed a significant amount of change between runs. This could either be the result of loss of fines or particle size change if improperly stored. No information about storage conditions was given.

Particle size determinations on several samples of the same material having differences in surface area, by air permeability, of 5 to 10% were made. The Micromerograph was capable of distinguishing between samples of relatively large materials (e.g. with 60 micron ground coal); however, the surface areas as calculated from the Micromerograph data were only 40 to 50% of those determined by permeability. The authors made no mention of this discrepancy, and no explanation was obvious.

The authors were quite concerned with the electrostatic charging of particles during the deagglomeration. They suggested the use of a radioactive gas in place of the pressurized nitrogen, or the use of a 5 milli-curie radiation source at the top of the column. They stated that even at its present stage of development the Micromerograph was far superior to other particle sizers and that, if a method for reduction of electrostatic charging of the particles was successful, the Micromerograph "may well represent the highest standard of achievement in the manufacture of accurate automatic particle sizing instruments." 8 references.

3.2.4 Evaluation of the Sharples Micromerograph for Particle Size Distribution Analysis, by Seymour M. Kaye, et al. Picatinny Arsenal, FRL-TR-54 (1962).

This report concluded that the Micromerograph does not properly evaluate either the coarse or the fine ends of the particle size distribution curve for a sub-sieve spherical glass bead sample. The bias at the coarse end was due to preferential hold up of coarser particles on the column walls, while at the fine end the authors thought that particles deposited were not recorded by the balance.

The Micromerograph was described. The particle size distribution of a standard glass bead sample (15 micron median, supplied by the Sharples Corporation) was determined. A consistent bias to the small side, compared to the Sharples standard curve, was demonstrated. These beads are usually used for checking and calibrating the Micromerograph. However, there appeared to be no effort to adjust the Picatinny unit to provide the proper distribution curve with these beads.

The balance-recorder system was evaluated in terms of accuracy, sensitivity, and the effect of deposit site on the balance pan. The balance was found to be accurate within $\pm 2\%$ (approx.) of the weight recorded. It was concluded that a weight change of 0.17 mg. could be detected by the system. It was also determined that there was no appreciable particle size distribution difference between different deposit sites on the balance pan. In determining the accuracy of the balance it was concluded by the authors that "no appreciable weight increase was observed after the 6.6 minute fall time, with a definite leveling off of approximately 16.5 mg. or 50% of full scale deflection. This posed several questions: was no further sample coming down after the 6.6 minute time period, or, if extremely fine particles continued to fall, was their weight insufficient to cause chart deflection?"

The above statement did not agree with a "typical run" illustrated in their Fig. 4. This figure indicated that 5 to 10% of the sedimentation was recorded after the 6.6 minute fall time. However, in spite of their "typical run" they concluded that no particles falling after 6.6 minutes were recorded by the balance and that this indicated some error in the standard templates furnished by the Sharples Corporation.

The next phase of the investigation dealt with the distance which the cloud of dispersed glass beads was forced down the column by the nitrogen blast used for deagglomeration. A transparent plastic column was substituted for the standard column, and a 64 frame per second motion picture camera was used to determine the particle fall. It was concluded that the particle cloud was forced down 34 centimeters, or approximately 15% of the column length, by the nitrogen blast. The authors stated that Stokes' Law calculations indicated that the Micromerograph template was corrected to compensate for this effect.

A microscopic study of particles examined after a fall time of 1.2 minutes (sedimentation time for a 17 micron particle) indicated the presence of particles approximately 2 microns in diameter. This was thought by the authors to be the result of incomplete deagglomeration, resulting in fine particles being carried down with the larger particles regardless of

settling time. It appears likely that a static attraction between the particles was responsible for the fine particles being carried down with these larger particles.

During the work with the aforementioned plastic column a deposition of particles on the inner walls of the column was observed. A microscopic examination was made of the original glass bead sample and of the material recovered on the balance pan after sedimentation. The material on the balance pan was reported to have a number average particle size of 8.0 microns, while the original material had an average of 11.3 microns. From this it was concluded that predominately coarser particles adhered to the column wall. This explanation was given for the instrument recording a finer distribution than was given by Sharples for this sample of standard beads.

The authors concluded that the Micromerograph was suitable for control purposes where reproducibility of results was of prime importance; however, its use as a tool for obtaining absolute particle size data was questionable.

- 3.2.5 An Evaluation of the Micromerograph, by Seymour M. Kaye, et al, Bull. 17th Mtg. JANAF, Panel on Anal. Chem., Sept. 1961, pp. 35-36 (Report classified; paper unclassified).

This article simply summarized the results of the previous report.

- 3.2.6 Particle Size Analysis of APC by Liquid Sedimentation, by E. K. Bastress, et al, AIAA Journal, 1, pp. 1182-1185 (1964).

The Mine Safety Appliances Particle Sizer, a centrifugal liquid sedimentation technique, was evaluated in comparison with the Micromerograph. The Micromerograph data were determined by Rohm and Haas, Redstone, and Thiokol, Elkton, on two different size samples submitted by Bastress. Samples of the same ammonium perchlorate were analyzed by Bastress using the Mine Safety Appliances particle sizer. With the fine

oxidizer, median about 10 microns, the two Micromerographs showed quite similar results, but both showed a long tail at the coarse end of the particle size which was not found with the MSA Analyzer. The authors ascribed this difference to failure of the Micromerographs to deagglomerate the sample properly. No data were given to indicate what deagglomeration settings were used. The agreement was quite poor between the two Micromerographs on the coarse material, median about 90 microns, with one Micromerograph indicating approximately 20% of the material to be larger than 200 microns and the other Micromerograph indicating virtually nothing larger than 150 microns. Again, no deagglomeration data were given. The authors stated that the difference between the Micromerograph and the MSA Analyzer was found probably because the large particles settling in the air were far out of the Stokes regime while the liquid sedimentation behavior was entirely within the Stokes regime. The authors apparently did not think highly of the Micromerograph. Their primary reference to an evaluation of the Micromerograph was the work reported by Seymore Kaye (3.2.4). The MSA particle size technique consists essentially of preparing a suspension of particles in a suitable fluid, transferring approximately one milliliter of this suspension to the centrifuge tube by means of a small feeding chamber, and observing the sedimentation rate using both normal gravity and centrifugation. Different fluids are used, depending upon the particle size to be measured. The liquid with which the initial suspension is made, the feeding liquid, is less dense than the liquid in which the sedimentation occurs. In the work reported here, benzene and di-n-butyl sebacate were used as the feeding liquids for the small and coarse materials, respectively, while chlorobenzene and diethyl phthalate were used for the sedimentation liquids.

The authors concluded that this sedimentation analysis technique was superior in speed, precision, and first cost to the Micromerograph, but that greater operational skill and judgement were required in its use.

3.2.7 Comments on "Particle Size Analysis of Ammonium Perchlorate by Liquid Sedimentation," by V. S. DeMarchi, AIAA Journal, 3, pp. 796-798 (1965).

This article consists primarily of the author's opinion of the previously summarized article. He said, "My own analysis of their reported distributions is in agreement with the results reported in the literature rather than those reported by Bastress, Hall, and Summerfield." The data of Bastress were replotted on log-probability paper. The author contended that the excess of coarse material above that expected in a log-normal distribution, was actually present in the form of agglomerated particles. DeMarchi stated that the MSA analyzer shows a deficiency of coarse particles, and that it was likely that these particles were missed by the "eyedropper" when sampling the dispersion in preparation for charging it to the sedimentation tube. As to the variation between several Micromerographs, the author indicated that it was very difficult to make comparative studies at different laboratories when using powders sensitive to their environment. He felt that the shape of the distribution curve obtained at Laboratory A showed that considerable agglomeration of the powder had occurred, whereas the data obtained at Laboratory B indicated that no caking was present. He stated that the preferred method of analysis would depend upon the use of the material and that both techniques, i. e. liquid sedimentation and Micromerograph, had advantages and disadvantages.

3.2.8 A Study of the Micromerograph as Applied to High-Fired UO_2 , by L. R. Phillips, Union Carbide Nuclear Company, Division of Union Carbide Corporation, Oak Ridge, Tenn. Report Y-1310, April 22, 1959 (Issued Sept. 28, 1960).

Two typical production batches of UO_2 were analyzed on three different Micromerographs, all at the same general location. One sample was nominally 3.5 microns, and the other nominally 4 microns; these are equivalent to 8-9 micron APC in fall time because of the density difference. The three Micromerographs gave very similar distributions on each of the lots, but the deviations between the instruments were of approximately the same

magnitude and direction within each of the UO_2 lots tested. It was noted that one instrument had been in operation for several years, a second for a few months, and the third for only a few weeks. The authors attached no particular significance to this fact. However, it seems entirely possible that these differences could be due to the differing amount of wear on the deagglomerator cones. A series of runs at varying deagglomerator gap and pressure settings was made with each of the UO_2 lots. In general there was little variation in sizes obtained when the deagglomerator gap was varied between 50 and 250 microns. However, generally speaking, sizes determined with 50 and 100 psi nitrogen pressure were larger than sizes determined with 200 to 300 psi nitrogen pressure at the same settings. Recoveries were generally low, ranging from 15 to 35%. A very interesting correlation was presented in which percent recovery was plotted against the product of gas pressure and slit width. Both variables were plotted on arithmetic coordinates. Although there was considerable scatter in the data, an increase in recovery was noted with an increase in the product of pressure and width. The material was recovered from the balance pan in all of the runs on one particular batch. After combination and blending, a particle size determination on this recycled material showed a coarser distribution than did the original sample run under the same conditions. The median increased from approximately 3.5 microns to nearly 5 microns. This difference was considerably greater than any of the other experimental variations reported.

The authors concluded that a particular Micromerograph gave reproducible particle sizes, that different instruments give slightly different results, and that a true distribution was not directly obtained but that results were biased in the direction of coarse particles. This latter conclusion was based upon their experimental evidence that the fine particles were preferentially held up in the instrument.

3. 2. 9 An Investigation of Potassium and Ammonium Perchlorate Size, by H. H. Nocke and C. E. McLean, Jr., Thiokol Chemical Corporation, Huntsville, Alabama. Bull. 8th JANAF Mtg. on Solid Propellants, 1952, Vol. II, pp. 67-77.

The authors discussed the effect of oxidizer particle size on burning pressure, physical properties, and processability of solid propellants. They mentioned that screen analysis was satisfactory for particles larger than 100 microns but that the Sharples Micromerograph was very useful for smaller particles. They discussed briefly the principles of the Micromerograph and described it as being erratic for the measurement of ammonium perchlorate particle size. They stated that although the deagglomerator produced a satisfactory dispersion of the oxidizer particles the particles reagglomerated because of static charges as they fell through the settling chamber. They found reagglomeration to be negligible when the air at the exit of the deagglomerator was ionized by an X-ray beam. They gave no data on the X-ray intensity used for this purpose, nor did they present any data to illustrate the change from erratic to reproducible behavior which they said resulted from this modification. They indicated that a 40°F change in room temperature would cause an apparent change of 3.5% in the Stokes diameter as a result of an increase in the viscosity of air. They reported good reproducibility between their Micromerograph and microscopic count on potassium perchlorate having a median size of approximately 50 microns. They found that the chamber pressure (i. e. burning rate) at a particular K for a standard motor and propellant had a strong correlation with the weight percent potassium perchlorate larger than the 37.8 microns.

3.3 Evaluations of the Coulter Counter

3.3.1 Development of Coulter Counter Techniques for Ammonium Perchlorate Particle Size Distribution Analysis, by J. H. Murphey, Jr., Thiokol Chemical Cor., Marshall, Texas. Bull. 19th ICRPG Working Group on Anal. Chem. Nov. 1963, pp. 277-285 (Report classified; article unclassified).

A Coulter Counter was purchased by Thiokol, Longhorn, for evaluation of APC size. A mixture of benzene and n-butanol saturated with lithium chloride was found to satisfy best the electrolyte requirements. Calibration of the Coulter Counter was accomplished with a glass bead

standard and with ragweed pollen. The Coulter Counter was found to be more precise than the Micromerograph for particle size distributions. The Coulter technique also was found to require less time than the Micromerograph. A difficulty was encountered in using the ragweed pollen normally suggested by the Coulter Company as a standard, since the alcohol used for an electrolyte dehydrated the pollen, causing it to shrink. After correcting for this size change, the Coulter Counter was found to agree with a Micromerograph generally; but it was found to have a bias toward a lower surface area of 300 to 400 cm^2/gm for materials having specific surfaces in the range of 1600 to 3800 cm^2/gm . No data on surface area or particle size distributions, however, were provided in the paper. The Coulter Counter was also compared with screen analysis for oxidizers in the range from 100 to 200 micron median sizes and found to be essentially identical. It was found that cleanliness had to be maintained around the Coulter Counter at all times. Dust and moisture had to be avoided, the electrolyte was stable up to only two weeks, and the noise level or background count was erratic at times.

3.3.2 Evaluation of Particle Size Distributions Obtained from Electrolytic Resistivity Changes, by R. R. Irani, Anal. Chem., 32, pp. 1162-1164 (1960).

The Coulter Counter was evaluated in comparison to microscopic measurement and liquid sedimentation techniques. Several operators and several Coulter instruments were used to measure glass beads, monocalcium phosphate, and flour. The three methods were found to agree well, even when spherical glass beads were crushed to provide highly irregular particles. It was found that in some cases certain, but not all, materials registered larger than their "true" size on the Coulter Counter. This was ascribed to undefined surface characteristics. By using a correction procedure described in the article, better agreement between the Coulter Counter and the "absolute" methods could be obtained.

3.3.3 Electronic Particle Size Analyses in the Subsieve Size Range, by W. S. Treffner and D. W. Robertson, Radex-Rundscheau, pp. 65-69 (1962).

Most of this article was concerned with the principle and the operating procedures of the Coulter Counter. Details of calibration procedure and development of satisfactory experimental procedures were included. The authors gave examples of particle size distributions of silicon carbide, alumina, chrome ores, and magnesites. There was no comparison of size data with other methods.

3.3.4 Preliminary Evaluation of the Coulter Counter Particle Size Instrument by Seymour M. Kaye, et al, Picatinny Arsenal, Dover, New Jersey. Technical Memorandum 1054, Oct. 1963.

This report followed the report written by the same authors on the Sharples Micromerograph (3.2.4), and the authors concluded that with glass beads the Coulter Counter was quite reproducible but had poor accuracy. The theory and operation of the Coulter Counter were discussed. An electrolyte of 1% aqueous sodium chloride was used, and the XC-3 glass beads were measured both with the microscope and the Coulter Counter. The standard ragweed pollen was also measured by both techniques. The precision of the Coulter Counter was determined by four runs on the same glass bead distribution. These had a precision of ± 0.4 microns for a geometric mean of 22.8 microns and a precision of ± 0.03 for a standard deviation of 0.70 microns. These numbers are essentially the same as previously reported for the Micromerograph (3.2.4). However, the particle size distribution obtained for the glass beads was in no wise comparable to the distribution obtained by the microscope. A weight mean diameter of 11.6 microns was obtained microscopically, with 22.8 microns obtained by the Coulter Counter. The 25% diameter showed even greater disparity, with a value of 20 microns by Coulter Counter and approximately 7 microns by microscope. It seems obvious that something was quite wrong with one or both of the particle size methods which was not apparent to the authors.

3.3.5 Assessment of Equipments for Automated Particle-Size Measurement, by H. C. Grant and R. Stenson, Explosives Research and Development Establishment, Waltham Abbey, Essex, England, TM No. 8/ M/ 65 (1965).

Several automatic particle counting systems were discussed. The theory and operating technique of the Coulter Counter were considered and an instrument was borrowed for evaluation. However, the authors indicated that no operating instructions were available, nor was there any literature based on past operational experience in Britain. Considerable difficulties in operation were encountered, including fibers and dust which choked the aperture, tiny bubbles were detected and counted, and temperature variations caused trouble with the Counter. The Coulter Counter apparently failed to record the smaller particles for sand, aluminum powder and glass beads, giving a coarser than expected size distribution. Ammonium perchlorate and zirconium powder were sized in an isobutyl/ ammonium thiocyanate solution, and particle sizes were "so grossly overestimated as to be meaningless." Many of these difficulties were probably due to inexperience and a lack of operating instructions.

3.4 Treatment of Particle Size Data

3.4.1 Statistical Description of the Size Properties of Non-Uniform Particulate Substances, by Hatch and Choate, J. Franklin Inst., 207, pp. 369-387 (1929).

This appears to be one of the first comprehensive references on the log-normal distribution. It discussed "skewed" distributions and indicated that when the logarithm of the particle size was used the distribution frequently became normal. It also discussed the equation of the log probability distribution:

$$n = \frac{\Sigma n}{\log \sigma_g \sqrt{2\pi}} e^{-(\log d - \log M_g)^2 / 2 \log^2 \sigma_g}$$

where

- n = number of particles of diam. d
- Σn = total number of particles
- M_g = geometric mean diameter
- σ_g = geometric standard deviation of the distribution

This log normal distribution will plot as a straight line on log probability paper using data obtained on either a weight or a number basis. For this type of a distribution the authors pointed out that the geometric mean diameter is obtained by reading the 50% size and that the geometric standard deviation is equal to the $\frac{\text{diameter at the 84.13\% point}}{\text{diameter at the 50\% point}}$ which is equal to the $\frac{\text{diameter at the 50\% point}}{\text{diameter at the 15.87\% point}}$. The authors concluded that the geometric mean and geometric standard deviation defined one and only one size frequency distribution curve, and that information concerning size distribution and relative frequency of certain sizes can be obtained from these two parameters. This particular reference is quoted in essentially all discussions of treatment of particle size data. 15 references.

3.4.2 The Distribution of Particle Sizes, by F. Kottler,
J. Franklin Inst., 250, pp. 339-356; 419-441 (1950).

This paper treated all particle size data as arising from either time oriented growth processes, as in photographic emulsions, or as time oriented size reduction processes such as crushing and grinding. Kottler indicated that the normal law could not be a size distribution law and through physio-chemical analogies that particle size data must of necessity follow a log-normal distribution. He indicated that even data which appear to fit normal distributions are more properly represented by a log-normal correlation. To properly fit a log-normal curve by eye he stated that all data outside the limits of 1 and 99% should be disregarded and that, of the remaining data, preference should be given to that nearest the 50% level. Calculation of a standard error for a log-normal probability curve using a chi-square-minimum-method was illustrated. Probit analysis, homogeneity of a distribution (all particles from the same population), and heterogeneous distributions (particles from several different populations) were discussed. 42 references.

3.4.3 The Goodness of Fit and the Distribution of Particle Sizes,
by F. Kottler, J. Franklin Inst., 251, pp. 449-514;
617-641 (1951).

This paper was built on the previous reference and

discussed the use of least squares and chi-square minimum techniques in determining the goodness of fit for a log-normal line to particle size data. In the latter part of the second portion of this paper, Kottler dealt with the subject of heterogeneity and indicated that different groups of particle size data should not be combined because of the danger of introducing several different distributions. He indicated a technique for determining whether or not two separate distributions were homogeneous and promised to deal with cases of heterogeneous distributions in a later paper. 15 references.

3.4.4 The Log-Normal Distribution of Particle Sizes: Homogeneity and Heterogeneity, by F. Kottler, J. Phys. Chem., 56, pp. 442-448 (1951).

In this article the author dealt with distributions made up of two log-normal distributions. From the data he indicated that the two distributions and their relative amounts could be calculated but did not indicate the method. He said, "obviously, we now have a representation of the data by means of 5 parameters," (the two intercepts, a_1 and a_2 , the two slopes, b_1 and b_2 , and c , which is apparently the ratio or percentage of one component). "The procedure for finding these 5 parameters," he said, "is similar to, but more complicated than that described in the case of homogeneity. Again, we start with the first 'guess' or approximation, denoted by one prime... The other values... can be found by means of a log probability chart in the manner which will not be described here in detail. Suffice it to say that the computation is similar to a problem of least squares with 5 unknowns." It might be added that these distributions look very similar to the ones obtained in grinding APC. 19 references.

3.4.5 The Interpretation of Abnormalities in the Log-Normal Distribution of Particle Size, by Riyad Irani, J. Phys. Chem., 63, pp. 1603-1607 (1959).

This article discussed a number of abnormalities in the log-normal distribution, including those with a finite maximum and/or minimum particle as opposed to the infinite maximum and minimum diameters present in the standard log-normal distribution. The author also discussed

distributions where the large and small particles had been removed from the distribution and mixtures of two distributions. He dealt at length with graphical techniques for determining the two components which make up these "compound distributions." These methods were also discussed at length in his book, Particle Size: Measurement, Interpretation and Application. 17 references.

- 3.4.6 Log-Normal Distribution in Breakage of Solids, by Benjamin Epstein, Ind. Eng. Chem., 40, pp. 2289-2291 (1948).

This article dealt with theoretical breakage of solid particles, especially coal, and showed that under normal conditions a log-normal distribution resulted. 19 references.

- 3.4.7 Better Control of Particle Sizes, by William Sholman, Chem. Eng., 69, No. 18, pp. 129-130 (1962).

This article dealt with log-normal distributions. The author indicated that with such a distribution a few data points were satisfactory for a complete description. Military standard MIL-A-192A for ammonium perchlorate was shown to represent a log-normal distribution. 10 references.

- 3.4.8 Methods of Representing Distribution of Particle Size, by J. B. Austin, Ind. Eng. Chem., 11, pp. 334-339 (1939).

The author presented three methods of representing particle size distributions. He discussed the logarithmic-probability correlation and plotted size data of a large number of different materials. He indicated that most particle size distribution data could be represented by a straight line using this correlation. He also indicated that if the size distribution by count plotted as a straight line on log-probability paper, the distribution by weight was a parallel straight line on the same coordinates.

The author also discussed arithmetic probability correlation, but indicated that particle size data fitted this distribution only occasionally, when the particles were produced by a chemical process, in which the particles tend to be a uniform size, rather than when materials were produced by crushing or grinding.

The third method discussed was the Rosin-Rammler relationship. It consisted of plotting the logarithm of the cumulative percent oversize on a log scale versus the size of particle on a log scale. A straight line plot indicates that the data fit the Rosin-Rammler distribution. It was suggested that this may be applicable to materials which are brittle and which contain minute cracks at which cleavage may start. The correlation does not seem to have the wide applicability of the log probability distribution. It may also apply to distributions which are more skewed than the log normal distributions. Formulas for calculating various average diameters and other parameters from the data were also included. 14 references.

3.4.9 The Analysis of Sieve Test Data, by J. W. Mullin,
Ind. Chemist, 36, pp. 272-278 (1960).

The author discussed determination of particle size by screening. He discussed such things as the ambiguity of mesh numbers without reference to wire thicknesses and type of screen. He also referred to the effect of variations in particle shape on apparent particle diameter, as determined by screens. The disadvantage of tabulation of data versus graphical analysis using both histograms and cumulative percentage curves with both arithmetic and logarithmic scales was discussed. He also dealt briefly with the log probability paper. A method of specifying particle size and distribution, termed the MA/CV designation, was proposed. The mean aperture, or MA, is the weight median diameter and the coefficient of variation, or CV, was expressed by $\frac{\sigma \times 100}{MA}$. There did not appear to be any particular advantage in using this technique over the weight median diameter and the standard deviation. The author referred to a symposium on particle size analysis, reported in the transactions of the Institute of Chemical Engineers, 1947 (special supplement to Vol. 25), which may be of interest. 5 references.

3.4.10 On the Proper Use of Transformations of Log-Normal
Functions in Small Particle Statistics, by A. Goldman, et al.
Los Alamos Scientific Laboratory of the University of California, Los Alamos, New Mexico. LA-3262, written

Dec. 1964 (Dist. Jul. 9, 1965).

This report was a detailed study of the log-normal distribution, with the apparent purpose of presenting a complete and uniform nomenclature as opposed to the varied and confusing notation in use up to the present. The report dealt primarily with the mathematical background of the log-normal distribution and is required reading to anyone dealing with the mathematics of particle size distribution.

- 3.4.11 Fitting Bimodal Particle Size Distribution Curves, by J. N. Dallavalle, C. Orr, and H. J. Blocker, Ind. Eng. Chem., 43, pp. 1377-1380 (1951).

The authors discussed bimodal frequency distributions and the theory of fitting these distributions with an equation. They presented several theories, including their proposal, referred to as the Selected Ordinate method. The examples which they picked were not represented well by the equations derived. 8 references.

- 3.4.12 An accurate Method for the Determination of the Components of a Heterogeneous Particulate Mineral System, by F. H. Goldman and J. M. Dallas Valle, Am. Mineralogist, 24, pp. 40-47 (1939).

This article dealt with the determination of relative amounts of several components in a mineral system. It had an interesting discussion of the effect of shape factor on the relationship between diameter and volume of a particle. 7 references.

APPENDIX A

The following is a list of Chemical Abstracts references not reviewed in the text of this report but which might be of interest to persons doing additional work on particle size measurement.

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<u>Page</u>	<u>Title and/or Summary</u>
1497c	Centrifugal Sedimentation in Cup Centrifuges for Particle Size Analysis of Extremely Fine Parameters: (less than 2-3 millimicrons)
3915f	Measuring Particle Size. Nine methods for measuring particle size, apparently in aerosols, are given with their respective applications, merits, and suitability.
5205c	Methods for the Particle Size Analysis of UO ₂ Powder and the Effect of Ball Milling on Size Distribution. <u>Powder Metallurgy</u> , 8, pp. 38-63 (1965), Ralph H. Steinberg. This article mentioned several methods of particle size determination, including sedimentation, the Coulter Counter, and optical microscopy, indicating certain advantages of the Coulter Counter.
5211f	Semi-automatic Set-up for Separate Count of Particles (Russian).
14396b	Characteristics of Automatic Particle Counter and Sizer (Japanese). Particle counter type EPC 2000 was described.

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2515d	Automatic Measurement of Specific Particle Size Ranges in Dust Mixtures. Methods of collecting dust particles of narrow particle size ranges were described. Apparently particles between 0.02 microns and 4.2 microns were involved.
2515e	Calculation of Particle Size Distribution in a Horizontal Elutriator. Equations are given for calculating the particle size distribution for a horizontal slit elutriator.

14147c Sedimentation Analysis with X-rays. Use of X-rays for determination of particle size by sedimentation without interruption by periodic sampling was described.

15438c Application of Radioisotopes to the Measurement of the Specific Surface and Particle Size of Powdered Materials. A Czechoslovakian article reviewing various sedimentation methods for determining particle size distributions by radioisotope methods.

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3944c Theoretical Principles of the Characterization of Powders, Distribution and Mean Characteristic Properties. A 6-page Yugoslavian article discussing particle size distribution and mean diameter. Incremental and cumulative methods of sedimentation analysis are critically reviewed.

8934e The Effects of Particle Size and Initial Temperature on the Deflagration of APC strands, by Larry Joseph Shannon (U. of Calif., Berkeley). University microfilms (Ann Arbor, Mich.) Order No. 64-5300, 118 pages.

10079a The Analytical Method of Calculation of Distribution Curves of Polydispersed Systems by the Rate of Settling of the Dispersed Phase of the Suspension (a foreign language article). The rate of settling of particles on the bottom of a hydrostatic balance pan immersed in this suspension is a satisfactory method for determining particle size distribution as tested on aluminum oxide and ferrous oxide powders.

C A 60

3740b Particle Size Analysis by Sedimentation. A Japanese article discussing particle size analysis by sedimentation in which the following problems are studied experimentally: measurement of the diameter of the powdered materials; selection of the dispersing agent; and the concentration and method of dispersion.

3953g The Coulter Counter. Pharm. Journal, 191, pp. 383-384 (1963). The applications of this apparatus in the measurement of particle size are discussed and the apparatus is described. Reproducibility of results in the filtration of normal saline and of a spore suspension in normal saline are shown in tabulated form.

- 5265f Laboratory Manual for Particulate Matter Analysis, by Paul H. Dutch (Fluor Corp., Ltd., Whittier, Calif.) U. S. Dept. of Commerce Office Technical Service, TB Report 162-953 67 pages (1959). Describes relatively simple but effective techniques for the identification of micron sized particles of metal, salts, fibers, and other organic materials which may be present in liquid rocket fuel system. U. S. Gov't. Research Report, Vol. 38(11), S-24 (1963).
- 7669b Thermal Decomposition of APC. A Japanese article discussing the effects of particle size, ambient atmosphere, and additives on the decomposition of APC. X-ray diffraction, gas chromatography, differential thermal analysis, and thermograms were used.
- 14733f Computation of Average Particle Size and of the Polydispersity Parameter. A Czechoslovakian article showing how computation may be used for evaluating particle size results obtained by sedimentation when the data follow a log-normal curve.
- C A 59
- No abstracts of interest.
- C A 58
- 1259f Determination of Surplus Areas of Sediments. Gas adsorption techniques were employed in the determination of the surface area. The theory was reviewed and a description given of a new apparatus and technique.
- 5061h Hindered Settling of Particles - Part IV. Precise Determination of Equations Describing the Hindered Fall of Monodispersed Spherical Particles. A Russian article describing the hindered settling of particles, shapeless particles, experimental verification of hypothesis of pseudo-particles and equations of hindered settling of shapeless particles. Various Reynolds numbers were considered.
- 6599f Comparison of Moment Measures for Sieving and Thin Section Data in Sedimentary Petrological Studies. The results indicated a 1:1 relation for mean grain size between sieving and thin section analysis.
- 14620f through 14621c The Properties of Dust, by A. G. Maris, Staub., 22, pp. 433-506 (1962). A discussion of dust, including various health problems, size measurement techniques, and electrostatic precipitation; particle sizes of 0 to 50 microns.

C A 57

- 2010f Theory of Coincidence in Coulter Particle Counter, Rev. Sci. Instr., 32, pp. 1132-1136 (1961). Discusses the probability of two or more particles occupying the sensing zone of the Coulter Counter simultaneously. Results are given for experimental testing of the theory with a monodispersed polystyrene latex.
- 4487c through 4488b A series of abstracts from Staub., 22, No. 3, pp. 77-144. These articles are on various aspects of particle size measurement and precipitation of dusts. Particle sizes appear to be below those of interest at present.
- 5669a Methods of Determination of the Specific Surface of Powders Used in the Production of Hard Alloys. A foreign language article, apparently Russian or Slavic, discussing a method of determining the specific surface of particles 100 micron and below requiring approximately 30 min. per determination.

C A 56

- 3313c Particulate Fluidization and Sedimentation of Spheres, by A. L. Loeffler and B. F. Ruth (Iowa State Univ., Ames) A.I. Ch. E. J., 5, pp. 310-314 (1959 - 20 references). Particulate fluidization and sedimentation data were taken over the Reynolds number range 0.005 to 1800 for glass spheres in both water and ethylene glycol.
- 4482e Techniques for the Evaluation of Powders. A series of three articles in Powder Met., 7, pp. 1-65, including a discussion of size, shape, diameter, structure, and hardness of metal powders.
- 4578c Sedimentation of Suspensions of Closely Sized Spherical Particles, by D. R. Oliver, Chem. Eng. Sci., 15, pp. 230-242. The Stokes stream function or flow past a single sphere is used to develop a relation between the volume concentration of solids in a suspension and the settling velocity. Experimental data from other sources are correlated.
- 9726g Fast Determination of Particle Distribution in Ceramic Raw Materials. A sedimentation apparatus was constructed, designed to reduce turbulence in the determination of the Andreasen particle distribution.
- 12700c Sedimentation of Irregular and Spherical Particles, Staub, 22, pp. 2-7 (1962). The preparation of glass spheres in the range 2 to 300 micron is described and the sedimentation measured. The sedimentation of non-spherical particles is compared to spheres.

C A 55

- 7790f Differential and Bi-differential Sedimentation Balances for Determination of Particle Size. A Swedish article discussing theory and design of sedimentation balances; some results obtained by means of the differential balance are discussed with reference to other methods of particle size determination.
- 9986f Determination of Particle Sizes of Less than 0.06 Millimeters. A foreign language article discussing sedimentation methods proposed by Andreasen, Delly, and Kopetski.
- 16025b Particle Size Measurement with an Improved, Continuously Recording Sedimentation Apparatus. Emil S. Palik, Anal. Chem., 33, pp. 956-959. An apparatus is described which measures the settling rate of particles in the range of 2 to 60 microns in a continuously recording manner by utilizing a torsion balance optical system. Particle size distribution results compare closely with the sieve analysis and two other sedimentation methods, whereas comparison with a counting method, which utilizes changes in electrolytic resistivity, shows a significant difference for one sample.
- 17118d The Use of Precision Micro-sieves in Particle Size Determination, Staub, 20, pp. 69-71 (1960). The Alpine Jet Sieve is used in determining particle sizes of fine powders, such as zircon dust and DDT.

C A 54

- 40108f Statistical Study of Small Particles. A French article which analyzes the distribution of particle size mathematically and develops formulas for it.
- 6209g Accurate Particle Size Distribution with Electro-formed Sieves. Anal. Chem., 31, pp. 2026-2028 (1959). A method is described for calibrating sieves. Particle size distributions in the range of 10 to 100 microns can be determined at 95% confidence limits of $\pm 9\%$ (approx.) for mean diameter.
- 9374i Problems in the Determination of Particle Sizes and in the Graphic Treatment of Particle Size Distribution According to Rosin, Rammler, and Sperling, by Werner Fritz. A German article discussing characterization of particle size distributions, available methods of determination, and sources of errors. The frequently used graphic presentation of particle size distribution according to Rosin, et al. is discussed.

- 14811a A foreign language article describing a new automatic recording sedimentation balance.
- C A 53
- 1891e Nomographs for Particle Size Analysis by Sedimentation and Permeability Methods. Reference to an article in an Indian journal.
- 8728i Particle Size and Surface Area Analysis, by Wm. H. Golod (Purdue Univ., Lafayette, Ind.) University Microfilms (Ann Arbor, Mich.). L. C. Card No. Mic. 58-7974, 173 pages.
- 1085a
through
1085d The Problem of Particle Size Measurement. References to an English journal. Available methods of particle size determination (gas permeability, light intensity, adsorption reflection, and bulk density measurements) are discussed. Comparisons are made, and possible uses and limits of the methods are analyzed. (16 references)
- 11904i Review and Evaluation of Methods of Particle Size Analysis, Part I, A definition of Terms and Classification of Sizing Methods. Part II, Sieve Analysis. Reference to Canadian bulletin, 83 pages. (69 references)
- 13695h Diameters of Particles in Chemical Engineering. Reference to a review of particle measurement, with 21 references in a foreign language journal.
- C A 52
- 835a Critical Review of Particle Size Determination by Means of Screen Analysis, Air Separation, Sedimentation, and the Blaine Test. A German reference recommending sedimentation in a range of from 1 to 60 microns; 9 pages, containing considerable data, and 13 references.
- C A 51
- 803g The Specific Surface Determination of Dispersed Bodies by the Air Penetrability Method (from a Russian periodical). The Beryagin Method for determining specific surface was found to be a universal method suitable for determining the specific surface of coarse and fine dispersions; it is based on the filtration of a highly rarified gas through the material. The apparatus is described in detail.

- 7803g Accuracy of Particle Size Determination by Cumulative Sedimentation Methods. Brit. J. of Appl. Phys., 7, No. 11, pp. 333-336 (1956).
- 10182a Fundamental Problems of Particle Size Measurements. An 8-page Japanese article discussing various particle size methods.
- C.A. 50
- 1553f New Method of Determination of the Size and Specific Surface of Powders Applied to Sintered Metals. Another reference to the technique listed under Vol. 51, p. 803g.
- 7647d Sources of Error in the Determination of Particle Size Distribution. A German reference discussing sampling, sample division, particle size analysis, effect of screening time, sample size, mesh size, and other screening equipment factors, agglomeration of particles during pre-treatment of samples and during analysis, and potential errors in the graphic presentation and evaluation of the analytical data. 40 references.
- 13517c Determination of Particle Size with a Simple Recording Sedimentation Balance. Anal. Chem., 28, pp. 1314-1316, Construction details are given for an automatic recording sedimentation balance. Good precision is obtained in the size range of 2 to 30 microns.
- C A 49
- 10684a Size Grading and Analysis, J. Chem. Educ., 32, pp. 326-328 (1955).
- C A 48
- 11850e Methods for Measuring the Particle Size of Fine Powders. A Japanese article reviewing particle size methods, with 31 references.
- C A 47
- 7810d Carbon Black Particle Size, Trans. Inst. Rubber Ind., 29, pp. 92-99 (1953). A discussion of electron microscopic measurements of particle size distributions in carbon black. The article discussed log-normal distributions and indicated that any two characteristics of a particle size, preferably mean particle diameter and specific surface, are sufficient to describe particle size and its distribution and consequently

the influence of any of these on the properties of vulcanized rubber mixtures. Any third size characteristic can be completely defined in the terms of these two.

C A 46

- 7832d Apparatus for Determining the Particle Size Distribution of a Powder, U. S. Patent 2,597,899, May 27, 1952. The patent for the Micromerograph.
- 7843h Particle Size Analysis from Sedimentation Curves. Discussions Faraday Soc., No. 11, pp. 15-27. Best results in particle size analysis requires visual observation of the particles. The frequency distribution is best calculated by an algebraic method based on the T-tables of Fischer and Yates (see Chem. Abstracts, 33, p. 1003⁶).
- 10702a Evaluation of Particle Size Analysis in Sieves. A German article discussing the various coordinate systems for the graphical representation of the results of screening analysis are explained and their mathematical background is discussed.
- 10702b Definition and Formularization of Screening Processes. A German article drawing attention to ambiguities in definition of particle size, average diameter, specific screening efficiency, and, in general, of terms used in screening analysis.

C A 45

- 2648g, h, i A volume entitled "Progress in Coal Science," with D. H. Bangham, Editor (British Coal Utilization Research Association), Interscience Publishers, Inc., NYC). The volume contains several articles with titles as follows:
 "Fine Powders and Particles in Industry" pp. 109-126.
 "Particle Size Measurement" pp. 127-147.
 "Assessment of Specific Surface of Powders and Porous Solids by Adsorption Methods" pp. 148-161.
- 6898d The Shape of Granulometric Distribution Curves, Antonio Giannone, U. of Naples, Ann. Chim. (Rome), 38, pp. 165-178 (1948). The fraction by weight of particles of mean diameter is

$$z = ax^K e^{-b/x} (Kx+b) / x^2$$

where a, K, and b are parameters adjustable to fit any known type of natural particle distribution. A graphic method is given for obtaining the specific surface from the above equation.

C A 44

No references.

C A 43

3687h Measurement of Particle Size, M. Chemist, 20, pp. 108-112 (1949). A review with 23 references.

5885h Errors in Routine Screening Tests, Chem. Eng. Mining Rev., 41, pp. 211-214 (1949). Variations in screening methods, in screens, in screening machines, and errors due to carelessness and other factors are noted and a number of recommendations given.

C A 42

423a Particle Size Distribution for the Entire Sub-Sieve Range. A sedimentation method to give distributions down to 1 micron, including manual weighing.

5633g Survey of Particle Size Methods, Ceram. Age, 50, pp. 155-157 (1947). A brief survey suggests the type of information obtainable and range of application for each method.

C A 41

2822f, g Some Practical Aspects of Particle Size Analysis in Industry, The Scope of Particle Size Analysis and Standardization, and the Sedimentation of Small Suspended Particles. Three articles from the Transactions of the Institute of Chem. Engineers (London) in 1947 survey. Various methods of determining particle size for industrial applications, the basic principles in sizing analysis and methods used, and the factors which govern the sedimentation rate of small particles are given.

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